

L141708



PATENT SPECIFICATION

NO DRAWINGS

L141708

Date of Application and filing Complete Specification: 18 Feb., 1966.

No. 7318/66.

Application made in United States of America (No. 434,137) on 19 Feb., 1965.

Complete Specification Published: 29 Jan., 1969.

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Index at acceptance:—C3 R(32D1, 32D6C, 32E2, 32E3, 32E4, 32FX, 32G2, 32H5F, 32H8, 32J1, 32J2Y, 32J3)

Int. Cl.:—O 08 g 21/04

COMPLETE SPECIFICATION

Curable Urethane Compositions

We, ALLIED CHEMICAL CORPORATION, a Corporation organised and existing under the laws of the State of New York, United States of America, of 61, Broadway, New York 6, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to curable urethane compositions, and compositions including chain extenders used therein.

It is well known that urethane elastomers can be prepared by reacting an essentially linear polymer, such as a polyester or a polyether, having terminal hydroxyl groups, with an excess of an organic polyisocyanate, which on reaction with the hydroxyl groups of the polymer forms an essentially linear urethane prepolymer having free isocyanato groups, and reacting this prepolymer with a bifunctional compound which may be a glycol, a diamine, an aminoalcohol, or a mixture of these. This bifunctional additive, on reaction with the excess isocyanato groups of the urethane prepolymer, serves to cross-link and/or extend the linear polymer chains to the point where the polymer becomes hard or rigid. Generally, the hydroxyl rich polymer and the organic polyisocyanate are combined initially to produce a urethane prepolymer containing free isocyanate (NCO) groups and subsequently this prepolymer is combined, usually with the aid of heat and pressure, with the bifunctional additive, i.e. the chain-extender. This latter step may be referred to as the curing step.

The curing step is carried out by admixing, and preferably by thoroughly blending, the prepolymer with the chain-extender usually at an elevated temperature. The mixture is then poured into suitable moulds and hardened, i.e. cured, by the application of heat and/or pressure, or the mixture may be masticated on heated rolls and formed into sheets.

[Price 4s. 6d.]

It has been observed that the mixture of prepolymer and chain-extender remains in a fluid, pourable state for a relatively short period of time, i.e. the curable urethane composition has a relatively short "pot-life", necessitating the preparation of such mixtures in small batches, which will fill only a small number of moulds. Since a process is generally considered uneconomical unless it can be effected on a large scale, prior art processes involving prepolymer/chain-extender mixtures have been found to be expensive, time-consuming, and inconvenient. Moreover, the short pot-life of these curable compositions makes the filling of moulds, especially those of intricate design, difficult and incomplete and it further results in the entrapment of gas bubbles in the thickened mass thus contributing to defective moulds. Another observation has been that the curable urethane compositions will not remain sufficiently fluid to be poured into moulds when the composition is maintained above ambient temperature for extended periods. In view of the fact that temperatures above ambient are necessary for the satisfactory preparation of the prepolymer and cured elastomer, this inadequacy adds to the difficulties of attaining economical large scale production.

This invention provides curable urethane compositions possessing a desirably long pot-life. The new compositions harden readily at relatively low temperatures yet remain in a fluid, pourable state for sufficient periods of time to permit adequate mixing of the urethane prepolymer and chain-extender and to allow the preparation of such compositions in relatively large quantities.

The invention is based on the surprising discovery that the pot-life of a curable urethane composition comprising a urethane prepolymer containing free isocyanato groups, and a chain-extender composed of a major proportion by weight of an aryl diamine, may be extended by the incorporation of an effective

amount of an organic tin compound. Since organic tin compounds are well known in the urethane art as catalysts, i.e. process accelerators, the anti-catalytic or decelerating effect exerted in the curable urethane composition of this invention cannot be explained nor can the necessity of imposing critical limits on the proportion of organic tin compound.

The curable urethane compositions of this invention are fluid and pourable when prepared and remain so for extended periods. On hardening, these compositions produce urethane elastomers having varied applications. They can be cast or moulded into intricate shapes and forms to produce such diverse articles as solid tyres, anti-vibration mountings, impellers, propellers, bushings, bearings, shaft linings, gears, belts, protective equipment, helmet linings, and gas masks.

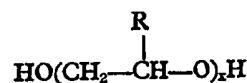
The urethane prepolymers, their mode of preparation, and the materials used in their preparation are known in the urethane art. Typically, the prepolymers are prepared by reacting, at a temperature between about 50° C. and 100° C., a hydroxyl-terminated polymer, e.g. a polyester polyol or a polyalkylene ether polyol, having an average molecular weight of at least 500 and a hydroxyl number of at least 40, with an excess of an organic polyisocyanate. Preferably an excess of at least one molar equivalent of isocyanate is used, although in some instances up to twelve or more equivalents of isocyanate per equivalent of hydroxyl group can be used. In the present instance prepolymers containing from 4% to 8% free isocyanato groups are especially preferred.

The hydroxyl-terminated polymer used to prepare the urethane prepolymer can be, for example a polyester polyol (including polyesteramide polyols) or a polyether polyol (including thiols). Preferably these polyols are essentially linear in character and have a functionality of about 2.

The polyester polyols, as a class, are well known and can be prepared by conventional means. For example such polyesters can be prepared by condensing one or a mixture of dibasic acids with one or a mixture of glycols. Typical of the suitable dibasic acids are succinic, glutaric, adipic, pimelic, suberic, azelaic, subacic, and terephthalic acids. Typical of the glycols which can be used are ethylene glycol, 1,2- and 1,3-propylene glycols, 1,4-butyleneglycol, and hexamethylene glycol. Polyesters derived from adipic acid and a mixture of ethylene and 1,2-propylene glycols are preferred. The polyesters can have an average molecular weight of at least 500, and preferably between 1000 and 2500, a hydroxyl number between 40 and 115, preferably between 50 and 70, and a low acid number, preferably below 5.

The hydroxyl-terminated polymer can also be a polyether polyol, of which broad class

the polyalkylene ether glycols are typical members. These glycols are well known in this art, several members being available commercially, and are believed to have the general formula



wherein R is hydrogen or a lower alkyl group and x is an integer of such magnitude that the molecular weight of the polyether glycol is at least 500 and preferably within the range of 1000 to 2500. Suitable glycols of this class include polyethylene ether glycol, polypropylene ether glycol, and polybutylene ether glycol. Polyether glycols of this class can be obtained by condensation of an alkylene oxide or mixture of alkylene oxides, such as ethylene oxide, propylene oxide and their mixtures with a polyhydric alcohol such as ethylene glycol, in the presence of a suitable catalyst, e.g. trimethylamine or potassium hydroxide. The preparation of such polyalkylene ether glycols is well known in this art.

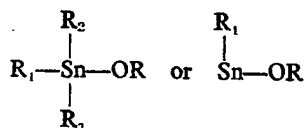
Any of a wide variety of organic polyisocyanates can be used to react with the polymeric polyols in the formation of the urethane prepolymer. Thus aromatic, aliphatic and cycloaliphatic isocyanates can be used. Liquid aromatic diisocyanates are preferred. As examples of this well known class of reactants, the following are mentioned: 1,4-phenylene diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 1,5-naphthalene diisocyanate, 4,4'-methylene-bis-(phenylisocyanate), cumene-2,4-diisocyanate, 4-methyl-1,3-cyclohexyldiisocyanate, 4,4'-methylene-bis-(cyclohexylisocyanate), 1,6-hexamethylene diisocyanate, and the polyalkylene-polyaryl polyisocyanates disclosed in United States Patent No. 2,683,730. Mixtures of these and equivalent isocyanates can be employed also if desired. Especially preferred is the commercially available mixture of about 80% 2,4- and about 20% 2,6-tolylene diisocyanates in pure or crude form.

The chain-extender which is included in the curable urethane composition is composed of a major proportion of an aryl diamine, a major proportion being defined as more than 50% by weight of the chain-extender. The chain-extender can contain 100% aryl diamine; however, other chain-extenders such as low molecular weight glycols and aminoalkanols, having from 2 to 10 carbon atoms, can be, and are preferably, included in the chain-extender composition in minor proportion, i.e. less than 50% by weight of the chain-extender composition. The aryl diamines are a well known class of urethane elastomer chain-extenders. These reagents, which are sometimes also referred to as "hardeners" probably react with the prepolymer by a cross linking mechanism thereby giving rise to a stiffening of the poly-

mer chain. The aryl diamines produce elastomers of excellent tensile strength, hardness, and other physical characteristics and hence are widely used. Typical examples of the aryl diamines are the following: 4,4'-methylene-bis-(2-chloroaniline), 4,4'-methylene-bis-(2-bromoaniline), 4,4'-methylene-bis-(2-methoxyaniline), 4,4'-methylene-bis-(2-hexylaniline), 4,4'-methylene-bis-(2-ethylaniline), 1,5-naphthalene diamine, 2,2'-dichlorobenzidine, and dianisidine. Mixtures of these and equivalent aryl diamines can also be used. Examples of the other components that can be used in addition to the aryl diamine component of the chain-extender composition are alkylene diols, such as ethylene glycol and 1,4-butane diol and aminoalkanols, such as 2-aminoethanol and 3-aminobutanol-1, and mixtures thereof.

The chain-extender is in general used in the curable urethane composition in a proportion of 5% to 25% based on the total weight of the composition and, preferably, from 10% to 20%, although other proportions may be desirable depending on the requirements for the elastomer.

The organic tin compounds in the new compositions are well known in the urethane art. In combination with the other components of the curable urethane composition of this invention and in the correct proportion, a decelerating rather than an accelerating effect is produced and an undesirably short pot life is extended to a desirably long pot life. The preferred proportion of organic tin compound is from 0.15% to 0.4% based on the total weight of the curable urethane composition, the optimum proportion generally being 0.20% to 0.35%. The organic tin compounds can be represented by the general formulae:



wherein R represents an acyl radical such as acetyl, propionyl, octanoyl, or lauroyl; R_1 , R_2 , and R_3 represent OR, alkyl of 1 to 18 carbon atoms, hydrogen, or halogen, R_1 , R_2 , and R_3 being the same, or different. Examples of organic tin compounds are as follows: dimethyltin dioctate, diethyltin diacetate, stannous laurate, stannous hexanoate, tributyltin o-phenylphenate, stannous octoate, stannous oleate, stannous tartrate, dibutyltin di(2-ethylhexoate), dibenzyltin di(2-ethylhexoate), dibutyltin dilaurate, dibutyltin bis(o-phenylphenate), dibutyltin bis(acetylacetonate), dibenzyltin dioleate, dibenzyltin dilaurate, diethyltin dilaurate, dilauryltin dibutyrate, dibutyltin dibutyrate, butyltin dibutyrate caproate, benzyltin tristearate, stannous succinate, and stannous adipate. Stannous octoate and

dibutyltin dilaurate because of their ready availability and effectiveness are preferred members of this class or organo-tin compound.

The term "an effective amount of an organic tin compound" as used in the definition of invention means the amount of a particular organo-tin compound which is effective when used with particular proportions of a specified urethane prepolymer and a specified chain-extender. In some cases it has been found that slight less or greater proportions of tin compound than the preferred amounts mentioned above give the unique results described.

It should be noted that where an organic tin compound is used as a catalyst in the formation of the prepolymer, which is a departure from the usual procedure, the amount of organic tin compound carried over in the prepolymer into the new curable urethane composition must be brought within the prescribed critical limits of this invention by adding or removing the organic tin compound as required, if the desired result of extender pot-life is to be obtained.

The chain-extender can be added to the urethane prepolymer containing free isocyanate groups in an amount which is generally within the range of 80% to 100% of the amount theoretically required to react with all of the free isocyanate groups of the prepolymer. The selection of a particular diamine, or mixture of diamine and glycol or aminoalkanol or other type of extender, is dependent to a large extent upon the properties desired in the cured elastomer. These criteria are thoroughly discussed in the many patents and publications in this field and hence, being well known to those skilled in this art, require no discussion here.

The invention includes within its scope compositions, adapted for use in making curable urethane compositions comprising a chain-extender composed of a major proportion of an aryl diamine together with an organic tin compound in an amount effective to provide a urethane composition with an extended pot-life. Such compositions give convenience in handling and shipment for use with conventional urethane prepolymers as described above.

The following Examples illustrate the invention. Parts and percentages are by weight and temperatures are given in degree Centigrade unless otherwise specified.

EXAMPLE 1

Part A—Preparation of Prepolymer

A urethane prepolymer was prepared in a conventional manner by heating at about 80° for about 3 hours, a mixture of 4,4'-methylene-bis(phenylisocyanate) and ethylene propylene adipate (a polyester derived from an 80:20 mixture of ethylene and propylene glycols and adipic acid, having an average mole-

cular weight of about 2000 and a hydroxyl number of about 56.1 mg. KOH per g. The diisocyanate and polyester were combined in amounts equivalent to 3.2 NCO groups to 1 OH group. The resultant urethane prepolymer contained 5.74% free NCO groups.

Part B—Preparation of a Curable Urethane Composition containing No Tin Salt.

A mixture of 5.75 parts of 4,4'-methylene-bis-(2-chloroaniline) and 1.75 parts of 1,4-butane diol were heated to 100° and then added to 70 parts of the urethane prepolymer, prepared as described in Part A preheated to 100°. The mixture was agitated for about 15 to 20 seconds and then poured into a mould preheated to 130°. The mixture has a pot-life of 70 seconds.

Part C—Preparation of a Curable Urethane Composition with Tin Salt

Repetition of the procedure of Part B of this example but with the inclusion of 0.24 parts (0.31%) stannous octoate resulted in a curable urethane composition having a pot-life of 220 seconds at 130°.

(Pot-life was determined by pouring the mixture into a mould preheated to the specified temperature and carefully observed. The time which elapsed from the mixing of the components until the composition was no longer fluid was taken as the pot-life. The fluidity of the mixture was determined by inserting a wooden tongue depressor into the curable composition. When the void formed by inserting and removing the depressor does not disappear, the mixture is said not to be fluid.)

EXAMPLE 2

Part A—A mixture of 7343 parts of polyoxypropylene diol (having an average molecular weight of 1000 and a hydroxyl number of about 110 mg KOH per g.) and 3272 parts of a mixture of about 80% 2,4- and about 20% 2,6-tolylene diisocyanates was heated to about 70° and maintained at between 59° and 83° for about 4½ hours. The resultant urethane prepolymer was cooled to ambient temperature. The product had an amine equivalent of 544 and contained 7.74% free NCO groups.

Part B—To 70 parts of the urethane prepolymer prepared in Part A and preheated to about 110°, 15.5 parts of molten (100°) 4,4'-methylene-bis(2-chloroaniline) were added and the mixture was vigorously agitated for about 15–20 seconds. The mass was poured into a mould preheated to 130°. The pot-life was 65 seconds.

EXAMPLE 3

A mixture of 7.58 parts of 4,4'-methylene-bis-(2-chloroaniline), 2.56 parts of 1,4-butane diol, and 0.20 parts (0.25%) of stannous octoate was heated to 100° and then added to

70 parts of hot (about 110°) urethane prepolymer prepared as in Example 2, Part A. The mixture was vigorously agitated for 15 seconds and then poured into a mould preheated to 130°. The pot-life of this curable urethane mixture was 240 seconds.

EXAMPLE 4

In a similar manner to that described in Example 2, a mixture of 15.5 parts of 4,4'-methylene-bis-(2-chloroaniline) and 0.24 parts (0.28%) of stannous octoate, when mixed with 70 parts of the urethane prepolymer described in Example 2, Part A, gave a curable urethane composition having a pot-life of 90 seconds.

EXAMPLE 5

A composition was prepared as in Example 4 but with the amount of stannous octoate increased from 0.24 parts to 0.37 parts (0.43%). The pot-life was reduced to 45 seconds.

EXAMPLE 6

A composition was prepared as in Example 3 but using a mixture of 9.3 parts of 4,4'-methylene-bis-(2-chloroaniline), 2.09 parts of 1,4-butane diol and 0.23 parts (0.28%) of stannous octoate. A curable urethane composition having a pot-life of 195 seconds at 130° was obtained.

EXAMPLE 7

A composition was prepared as in Example 3 but using 11.6 parts of 4,4'-methylene-bis-(2-chloroaniline), 1.3 parts of 1,4-butane diol and 0.24 parts (0.29%) of stannous octoate. A curable urethane composition having a pot-life of 110 seconds at 130° was obtained.

EXAMPLE 8

Example 7 was repeated using 0.18 parts (0.22%) of stannous octoate instead of 0.24 parts. A curable urethane composition having a pot-life of 95 seconds at 130° was obtained.

EXAMPLES 9–13

Part A—Prepolymer Preparation
A mixture of 500 parts ethylene-propylene adipate (molecular weight 2000, hydroxyl number 56.1) and 85 parts of a mixture of about 80% 2,4- and about 20% 2,6-tolylene diisocyanates was heated to and maintained at 80° for 3 hours.

In a separate vessel 31 parts of ethylene glycol were added dropwise, at 90° to 95°, to 183 parts of hot (85° to 90°) mixed 2,4- and 2,6-tolylene diisocyanates. The resultant mass was heated at 90° to 95° for ½ hour after completion of the glycol addition. 146 parts of the resultant adduct were then added to the polyester prepolymer mass prepared above and the mixture heated at 80° for three hours. The resultant prepolymer contained 6.2% free NCO.

Part B

Curable urethane compositions were prepared using 70 parts of the urethane prepolymer of Part A, a 50%—50% mol equivalent mixture of 4,4'-methylene-bis-(2-chloro-aniline) (6.2 parts) and 1,4-butane diol (2.1

parts), and zero or various amounts of organic tin compound. The effects of the tin compound concentration on the pot-life of the resultant curable urethane compositions are indicated by the data in the following Table.

TABLE

Example	Tin Compound	Parts	Concentration % of Total	Pot-Life (Seconds)
9	none	—	0	75
10	A	0.227	0.29	180
11	B	0.227	0.29	150
12	A	0.109	0.14	75
13	A	0.344	0.44	60

Legend: A is dibutyltin dilaurate

B is stannous octoate

WHAT WE CLAIM IS:—

1. A curable urethane composition comprising a urethane prepolymer containing free isocyanate groups, a chain-extender composed of a major proportion by weight of an aryl diamine, and an amount of an organic tin compound effective to provide a urethane composition with an extended pot-life.

2. A curable urethane composition as claimed in claim 1 comprising from 0.15% to 0.40% by weight of the organic tin compound.

3. A curable urethane composition as claimed in claim 2 comprising 0.20% to 0.35% by weight of the organic tin compound.

4. A curable urethane composition as claimed in any one of the preceding claims comprising 5% to 25% by weight of the chain-extender.

5. A curable urethane composition as claimed in any one of the preceding claims wherein the chain-extender is composed of a major proportion by weight of an aryl diamine and a minor proportion by weight of a glycol or aminoalkanol.

6. A curable urethane composition as claimed in any one of the preceding claims wherein the organic tin compound is stannous octoate or dibutyltin dilaurate.

7. A curable urethane composition as claimed in claim 1 substantially as described in any one of the foregoing Examples 1, 3, 4, 6, 7, 8, 10, and 11.

8. A composition adapted for use in a curable urethane composition comprising a

chain-extender composed of a major proportion by weight of an aryl diamine together with an organic tin compound in an effective amount to provide a curable urethane composition with an extended pot-life.

9. A composition as claimed in claim 8 comprising the organic tin compound in an amount sufficient to provide 0.15% to 0.40% by weight of organic tin compound in the curable urethane composition.

10. A composition as claimed in claim 9 wherein the organic tin compound is present in an amount sufficient to provide 0.20% to 0.35% by weight of organic tin compound in the curable urethane composition.

11. A composition as claimed in any one of claims 8 to 10 wherein the chain-extender is composed of major proportion by weight of aryl diamine and a minor proportion by weight of a glycol or aminoalkanol.

12. A composition as claimed in any one of claims 8 to 11 wherein the organic tin compound is stannous octoate or dibutyltin dilaurate.

13. A composition as claimed in claim 8 substantially as described.

14. A process for the preparation of a curable urethane composition the process comprising adding to a urethane preformed prepolymer containing free isocyanate groups, a chain-extender composed of a major proportion by weight of an aryl diamine, and an amount of an organic tin compound effective to provide a urethane composition with an extended pot-life.

15. A process as claimed in claim 14 where-

in 0.15% to 0.40% by weight of the organic tin compound is employed.

5 16. A process as claimed in claim 15 wherein 0.20% to 0.35% by weight of the organic tin compound is employed.

17. A process as claimed in any one of claims 14 to 16 wherein 5% to 25% by weight of the chain-extender is employed.

10 18. A process as claimed in any one of claims 14 to 17 wherein the chain-extender is composed of a major proportion by weight of an aryl diamine and a minor proportion by weight of a glycol or aminoalkanol.

19. A process as claimed in any one of

claims 14 to 18 wherein the organic tin compound is stannous octoate or dibutyltin dilaurate. 15

20. A process as claimed in claim 14 substantially as described in any one of the foregoing Examples 1, 3, 4, 6, 7, 8, 10 and 11. 20

21. A curable urethane composition whenever prepared by a process as claimed in any one of claims 14 to 20.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1969.
Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which
copies may be obtained.